

Polymer Pyrolysis and Oxidation Studies in a Continuous Feed and Flow Reactor: Cellulose and Polystyrene

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A dual-zone, continuous feed tubular reactor is developed to assess the potential for formation of products from incomplete combustion in thermal oxidation of common polymers. Solid polymer (cellulose or polystyrene) is fed continuously into a volatilization oven where it fragments and vaporizes. The gas-phase polymer fragments flow directly into a second, main flow reactor to undergo further reaction. Temperatures in the main flow reactor are varied independently to observe conditions needed to convert the initial polymer fragments to CO₂ and H₂O. Combustion products are monitored at main reactor temperatures from 400 to 850 °C and at 2.0-s total residence time with four on-line GC/FIDs; polymer reaction products and intermediates are further identified by GC/MS analysis. Analysis of polymer decomposition fragments at 400 °C encompasses complex oxygenated and aromatic hydrocarbon species, which range from high-molecular-weight intermediates of ca. 300 amu, through intermediate mass ranges down to C₁ and C₂ hydrocarbons, CO, and CO₂. Approximately 41 of these species are positively identified for cellulose and 52 for polystyrene. Products from thermal oxidation of cellulose and polystyrene are shown to achieve complete combustion to CO₂ and H₂O at a main reactor temperature of 850 °C under fuel-lean equivalence ratio and 2.0-s reaction time.

Introduction

Oxyhydrocarbon and hydrocarbon polymers such as cellulose, polystyrene, and polyethylene constitute a significant proportion of municipal solid waste. In the United States, cellulose as the main component of paper contributes approximately 39% by mass and plastics contribute approximately 9% by mass to municipal solid waste (1). Cellulose is also a major component of the various forms of biomass. Although these materials are useful as fuels in incineration processes and refuse-to-energy conversion due to their relatively high heat value, environmental concerns

exist over possible products resulting from incomplete combustion in municipal waste incinerators (2–5).

A number of studies on thermal and oxidative decomposition of polymers have reported valuable data on products or overall rates of polymer volatilization and reaction under non-steady-state operating conditions. Many of these studies are based on experiments that use a batch or a semibatch reactor with continuous gas flow and batch polymer inlet, drop tube furnace, or temperature-programmed gravimetric analysis. The batch reactors report valuable product formation data but do not determine simultaneous time of formation and fuel equivalence in the vapor phase and are often operated at high initial fuel equivalence. A drop tube furnace monitors mass loss and ignition characteristics of a particle, in addition to intermediate product formation, but time of vapor-phase species reaction can vary from flow through the reactor to formation on exit. Global kinetics of polymer volatilization is determined by thermal gravimetric analysis, which can monitor mass loss and products as the initial mass is exposed to a temperature ramp (6–9). Thermal gravimetric studies are valuable in determining temperature regimes of polymer reaction, transformation, and volatilization, in addition to intermediate product identification.

Previous Studies: 1. Cellulose. Studies on pure cellulose pyrolysis and oxidation fall into general categories of low and high temperatures. There are few studies on pure cellulose at temperatures over 700 °C in the literature due to its low heating value and oxygenated structure. Pastorova et al. (10) report an extensive list of products from the pyrolysis of cellulose, which is initially charred at 190–390 °C and then further reacted at temperatures of 610 and 770 °C. They report that aromatic compounds increase with an increase in char temperature. Keating and Gupta (11) investigated the oxidative pyrolysis of cellulose at temperatures between 1500 and 2900 K at identical fuel equivalence ratios in air and in O₂. They observe larger quantities of the identified products from pyrolysis and oxidation in air, relative to that in O₂. They recommend a cellulose combustion process of initial pyrolysis and then stages of oxidation and pyrolysis for minimization of intermediate products and NO₂ formation.

A number of studies have been reported on cellulose pyrolysis and combustion at temperatures below 700 °C, and these consistently show similar intermediate product distributions (12–15). Pouwels et al. (12) identified a wide range of gas-phase products from Curie-point pyrolysis coupled with gas GC/MS at 510 °C under batch conditions. Jakab et al. (13) focus on thermal decomposition products from cellulose and wood effected by the presence of solvents when their reactor is heated to 400 °C at 20 °C/min. Shafizadeh (14) studied cellulose pyrolysis from below 300 to over 500 °C. He reports acceptable conversion to desired products (light hydrocarbons, levoglucosan, anhydro sugars, oligosaccharides, pyrans, and furan dehydration species) is obtained between 300 and 500 °C.

Suuberg et al. (6) and Milosavljevic and Suuberg (7) conducted a number of studies on cellulose pyrolysis. They conclude from thermal gravimetric analysis (TGA) experiments and literature data that cellulose exhibits two different activation energies in its decomposition. One value reported for overall decomposition is 140–155 kJ/mol, which is observed with both low and high heating rates and *T*-ramps to temperatures above 327 °C. A second value of about 218 kJ/mol applies for decomposition with lower heating rates to temperatures below 327 °C. They conclude that the occurrence of different activation energies is due, in part, to

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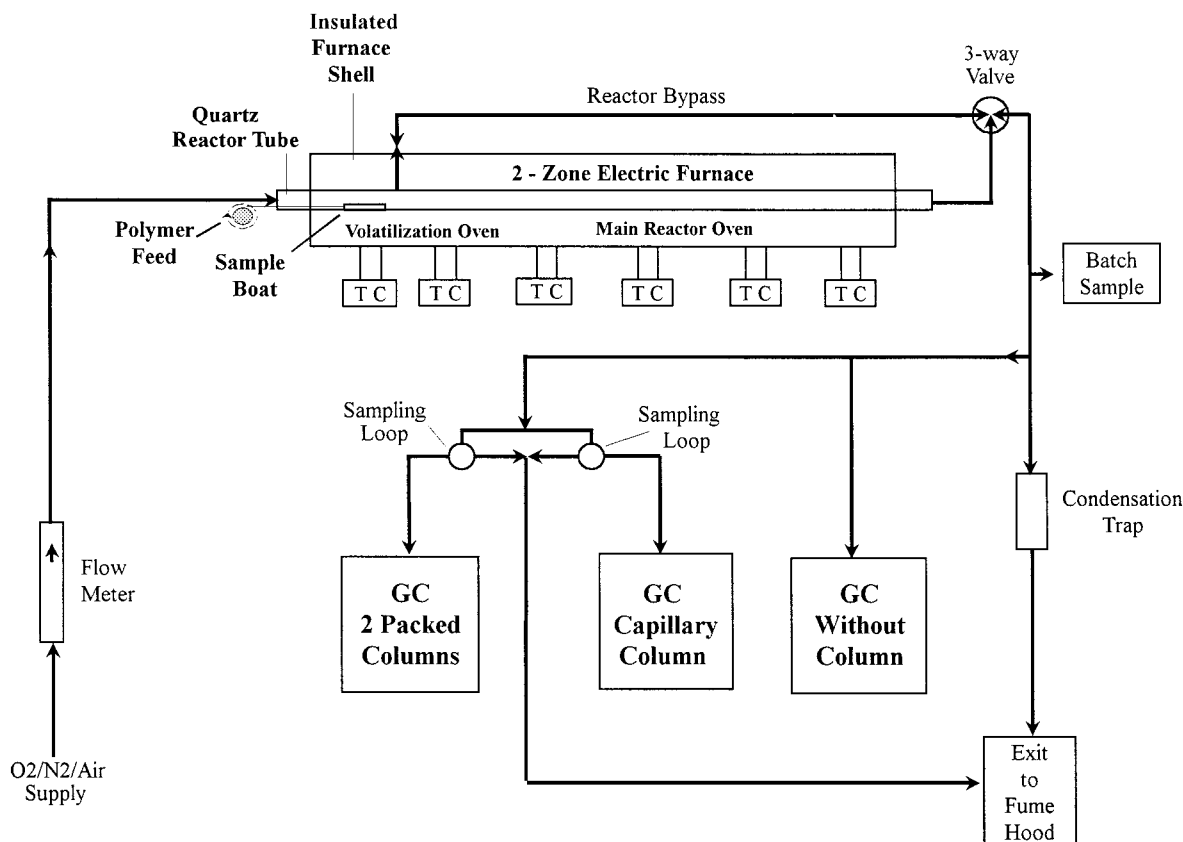


FIGURE 1. Two-zone oven, continuous feed experimental apparatus. TC denotes a thermocouple and proportional controller pair providing temperature control for the electrical oven heaters.

the role of relatively high-molecular-weight products, or tars, and that the actual kinetics is more complex than can be described by an overall process.

Several research groups investigated thermal decomposition of biopolymers, of which cellulose is an important fraction, over a range of temperatures (16–21). Funazukuri et al. (16) measured weight loss and product yields (C_6 species and below) from the flash pyrolysis of cellulose powder, cellulose particles, and filter paper under batch conditions. Reaction temperatures and heating interval ranged from 310 to 770 °C and from 0.5 to 20 s, respectively. They report that CO yields increase with weight loss and pyrolysis temperature. CO_2 yields are proportional to weight loss but are independent of pyrolysis temperature. Encinar et al. (17) used a tubular reactor containing a batch sample of polymer to study gaseous effluent from olive and grape bagasse. Gas concentrations were measured at temperatures from 300 to 900 °C. The gaseous products and solids from combustion were observed to decrease with increasing temperature. Studies by McKenzie, Lipari, Williams, and Pakdel all report that products from thermal degradation of biomass are similar to those observed in cellulose pyrolysis and oxidation (18–21).

2. Polystyrene. A number of studies have been reported on the thermal decomposition of polystyrene at temperatures from 700 to 1200 °C (22–28). Levendis's group (22–24) report data on decomposition of polystyrene in horizontal batch reactors and in drop tube furnaces, with gas-phase and particulate samples collected on glass fiber filters or XAD adsorbents. Polymer particles allowed to burn under flame conditions show formation of soot and high levels of PAHs.

Durlak et al. (25) studied the combustion of polystyrene spheres in an upflow tubular reactor with 0.5-s residence time over a temperature range of 800–1200 °C. They reported that the total PAHs and mass of the combined gas-phase and

particulate effluent decrease with increasing temperature and with decreasing polymer particle size. They indicate that polystyrene produces more soot and PAHs than other polymer plastics and recommend polystyrene be burned under conditions of high excess air to minimize emission of these species.

The research group of Karasek (26) identified a number of polyaromatic hydrocarbons from their high-temperature (850–950 °C) batch feed (2 g) pyrolysis and oxidation flow tube experiments. The gas velocity through their reactor was slow, ca. 12 cm/s, with products collected in cryogenic traps and on glass-wool filters. Elomaa and Saharinen (27) performed similar experiments with smaller samples, collecting soot in addition to analyzing the soot extracts for PAHs.

Many investigators have examined the pyrolysis and oxidation of polystyrene at temperatures between 200 and 550 °C (29–35). Brauman et al. (29) investigated the thermal degradation of vertically mounted polystyrene rods under radiant heating and nonflaming conditions at 446 °C in air and in nitrogen. They report average styrene monomer yields of 33% from reaction under nitrogen and relative concentrations of high-boiling-point products: styrene > trimer > dimer > tetramer > pentamer > hexamer. Shapi and Hesso (32) studied thermal decomposition of polystyrene at 300 °C using a Pyrex pyrolysis tube under synthetic air or nitrogen. They extracted vapor-phase products in a hexane solvent trap and report 164 volatile species from reaction in air and 71 in nitrogen. Relative product yields were 86.8% in air and 90.3% in nitrogen, with relative yield percents of styrene (27.3%) > benzaldehyde (14.7%) > dimer (8.2%) > trimer (3.1%) in air. Carniti et al. (35) studied thermal degradation of polystyrene and resulting products from batch reaction in a vacuum-sealed glass vial, at temperatures to 420 °C. The thermal degradation of polystyrene was reported to follow

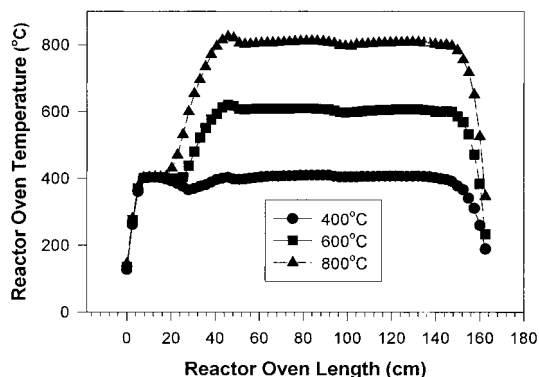


FIGURE 2. Reactor temperature profiles at 2.0-s residence time.

first-order kinetics in the initial part of the reaction up to 300 min.

Present Study. Results on conversion and product formation from thermal oxidation of cellulose and polystyrene as a function of temperature using a continuous flow reactor at known reaction time and fuel equivalence ratio (ϕ) are described in this study. The reactor has two isothermal reaction zones in series: a volatilization oven into which polymer and air are fed and a higher temperature zone to study reaction (oxidation/pyrolysis) of the volatilization products. Analysis of initial, intermediate, and final products as a function of temperature, at known ϕ and reaction time, allows one to identify conditions for complete conversion of polymer fragments to CO_2 and H_2O . The apparatus includes a continuous monitor of vapor-phase products to ensure uniform, steady-state operation. The continuous feed, temperature, ϕ , and residence time parameters are all relevant to operation of practical municipal solid waste incinerators.

Experimental Section

Reactor. The apparatus consists of a horizontal tubular flow reactor with on-line analytical train, as shown in Figure 1. The quartz reactor tube is 2.0 m in length, is 1.05 cm in inner diameter, and is surrounded by cylindrical electrical heaters (Thermcraft Co.) distributed over the two adjacent oven zones. The first zone, or volatilization oven, has a 7.6-cm long heater on the inlet side followed by a 20.3-cm long heater. The shorter heater is used to provide higher heat flux to compensate for heat loss at the reactor inlet and brings the incoming air and polymer feed up to temperature quickly. The longer heater serves to maintain a uniform temperature throughout the volatilization oven and allows the initial vapor fragments to pass into the second zone without condensation.

The second oven zone is the main reactor; it has two central 46-cm long heaters and two 20.3-cm end heaters. Effluents pass from the main reactor to the analytical train through Pyrex and stainless steel transfer lines that are heated to 220 °C. The volatilization oven temperature is fixed at 400 °C. The main reactor temperature is held constant (± 10 °C) and is controlled in the range 400–850 °C, with 2.0-s vapor residence time.

The volatilization oven and main reactor heaters are controlled by proportional controllers (Jenco Co.) with K-type thermocouples (Omega Engineering Inc.). Uniform temperature profiles, in both time and distance along each reactor zone, are readily achieved within ± 10 °C (see Figure 2). The heaters are usually operated at about one-half of their maximum rated power to limit temperature over-run and oscillation. This limits the main reactor temperature to a maximum of 1100 °C, which is in the range of the flue gas temperatures of municipal solid waste incinerators (3, 4).

Polymer Feed. The continuous polymer powder feed mechanism consists of a small diameter open-top or U-

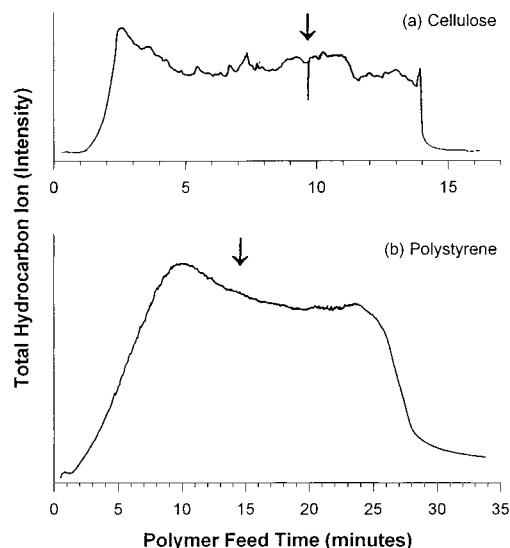


FIGURE 3. GC/FID signal from the total hydrocarbon versus time indicating closeness to steady-state operation of the reactor. Arrows indicate inlet of sample to GCs.

channel tube of about 20-cm length made of quartz or stainless steel; it is filled with a uniform distribution of polymer powder at a known bulk density. This U-channel "boat" is fed slowly into the volatilization oven by connection to a variable drive syringe-pump (Sage Industries/Orion Research Inc.) with a 2-mm diameter stainless steel rod. The feed rod passes through a septum at the upstream end of the reactor tube in order to seal the reaction zones from outside air. The feed rates are around 55 mg/min for cellulose and 8 mg/min for polystyrene and are sufficient to allow steady-state conditions. The volatilization oven heaters are adjusted to maintain a uniform temperature between 350 and 450 °C.

Reagents. The polymer powder reagents used were microcrystalline cellulose (Sigma Sigmacell type 101); polystyrene (Aldrich Chemical Co.) with average molecular weight 230 000, melt index 8.5, particle density 1.04 gm/cm³, and particle size in the range 0.1–0.3 mm.

Gas Flow. Dry air was inlet to the reactor tube 30 cm upstream of the initial volatilization oven heater and flowed over the polymer within the U-channel boat and through the reactor at a known flux. With a fixed 2.0-s gas residence time in the main reactor, the flow Reynold's number was in the range 70–170. This ensured that the flow was within the laminar regime throughout the reactor and that there was no tendency for the flow to lift unvaporized polymer particles into the reactant stream.

A second method of gas flow incorporated a small nitrogen flow over the feed polymer, with the main air plus supplemental oxygen inlet separately via a Tee. These streams met and mixed in the volatilization oven, and the initial $\text{O}_2:\text{N}_2$ ratio was always 21:79. The N_2 stream prevents back-diffusion of the oxidation or flame radical pool to unfed polymer and preignition of the feed polymer, which was observed in polymer mixture reaction studies where the solids exhibited lower melting points.

Analysis. The analytical train consists of three on-line gas chromatographs using flame ionization detectors (GC/FIDs). The first GC (Varian 3700) uses two 3-mm diameter packed columns with two gas sample injectors and two FIDs. CO and CO_2 are methanated using a ruthenium catalyst and hydrogen-reducing agent to provide high sensitivity by a FID after separation on a Carbosphere packed column (Alltech Associates Inc.). The second column in this GC is a Super-Q packed column (Alltech) which separates the light hydrocarbon species from C_1 to C_4 . The second GC (Hewlett-

TABLE 1. Distribution and Fate of Vapor-Phase Products in the Oxidation of Cellulose^a

no.	MW	products	main reactortemperature (°C)							
			400	450	500	550	600	650	700	750
1	16	methane, CH ₄	x	x	x	x	x	x		
2	28	ethene, C ₂ H ₄	x	x	x	x	x	x		
3	30	ethane, C ₂ H ₆	x	x	x	x	x	x		
4	42	propene, C ₃ H ₆	x	x	x	x	x	x		
5	44	acetaldehyde, C ₂ H ₄ O	x	x	x	x	x	x		
6	56	butene, C ₄ H ₈	x	x	x	x	x	x		
7	68	furan, C ₄ H ₄ O	x	x	x	x	x	x		
8	58	acetone, C ₃ H ₆ O	x	x	x	x	x	x		
9	72	2-butanone, C ₄ H ₈ O	x	x	x	x	x			
10	82	2-methylfuran, C ₅ H ₆ O	x	x	x	x	x			
11	78	benzene, C ₆ H ₆	x	x	x	x	x	x	x	
12	96	2-ethylfuran, C ₆ H ₈ O	x	x	x					
13	96	2,5-dimethylfuran, C ₆ H ₈ O	x	x	x	x				
14	84	3-penten-2-one, C ₅ H ₈ O	x	x	x	x				
15	92	toluene, C ₇ H ₈	x	x	x	x	x			
16	84	3H-furan-2-one, C ₄ H ₄ O ₂	x	x	x					
17	100	3-hexen-1-ol, C ₆ H ₁₂ O	x	x	x					
18	96	3-furfural, C ₅ H ₄ O ₂	x	x	x	x	x			
19	96	2-furfural, C ₅ H ₄ O ₂	x	x	x	x	x			
20	98	2-furanmethanol, C ₅ H ₆ O ₂	x	x						
21	114	3-hexyne-2,5-diol, C ₆ H ₁₀ O ₂	+							
22	98	5-methyl-2(3H)-furanone, C ₅ H ₆ O ₂	x	x	x					
23	96	cyclopent-2-ene-1,4-dione, C ₅ H ₄ O ₂	x	x	x					
24	104	styrene, C ₈ H ₈	x	x	x	x	x			
25	96	2-methyl-2-cyclopenten-1-one, C ₆ H ₈ O	+	x	x					
26	84	5H-furan-2-one, C ₄ H ₄ O ₂	x	x	x	x	x			
27	96	2-cyclohexen-1-one, C ₆ H ₈ O	x	x						
28	112	3-methyl-2,5-furandione, C ₅ H ₄ O ₃	x	x						
29	110	5-methyl-2-furfural, C ₆ H ₆ O ₂	x	x	x	x				
30	94	phenol, C ₆ H ₆ O	x	x	x	x				
31	118	2,3-benzofuran, C ₈ H ₆ O	x	x	x	x	x			
32	112	3,4-dihydro-6-methyl-2H-pyran-2-one, C ₆ H ₈ O ₂	x	x						
33	112	2-hydroxy-3-methyl-2-cyclopenten-1-one, C ₆ H ₈ O ₂	x	x						
34	124	2-methyl-1,4-benzenediol, C ₇ H ₈ O ₂	x	x	x	x				
35	126	3-(hydroxy)-2-methyl-4-pyrone, C ₆ H ₆ O ₃	x	x						
36	144	5-(hydroxymethyl)-2-tetrahydrofurfural-3-one, C ₆ H ₈ O ₄	x	x	x					
37	144	1,4:3,6-dianhydro-α-D-glucopyranose, C ₆ H ₈ O ₄	x	x	x					
38	126	5-hydroxymethyl-2-furfural, C ₆ H ₆ O ₃	x	x	x					
39	162	1,6-anhydro-β-D-glucose, C ₆ H ₁₀ O ₅	x	x						
40	28	CO	x	x	x	x	x	x	x	
41	44	CO ₂	x	x	x	x	x	x	x	x
fuel equivalence ratio (φ)			0.21	0.21	0.21	0.22	0.22	0.25	0.27	0.28
carbon mass balance (%)			61.76	69.17	73.68	82.40	88.18	88.71	95.53	93.12

^a Volatilization oven temperature 400 °C, main reactor temperature as indicated; x signifies detected by GC and GC/MS analysis, + signifies detected by GC/MS and not detected by GC.

Packard 5890 series II) is fitted with a capillary column for separation of gas-phase products over C₅. For studies on cellulose the capillary column is an Alltech Associates Inc. AT-5 (SE-54) 1.2-μm, 30-m × 0.53-mm column, while for studies on polystyrene a J & W Scientific DB-1 (SE-30) 1.2-μm, 15-m × 0.53-mm column is used. A capillary column with the same liquid phase is used for identification of gas-phase products in the GC/MS (Varian 3400 gas chromatograph with Varian Saturn II ion trap mass spectrometer).

The third GC (Varian 3700) operates without column packing and uses reactor effluent for carrier at 250 °C. Its FID is used to measure total hydrocarbon and oxyhydrocarbon products. This signal serves as an important monitor on uniform, steady-state operation. It monitors continuity of total operation: gas flow, polymer feed, volatilization rate, absence of preignition, reaction, product effluent, and product transfer to analytical equipment. Figure 3 shows a typical total hydrocarbon signal from this FID against time for the approximate 15–30-min duration of an experimental run with cellulose and polystyrene. This continuous monitoring of total hydrocarbons also serves as a second measurement on destruction efficiency and supports quantitative results obtained by the other three GC/FIDs.

Identification of reaction products includes matching of retention times against known standard compounds under identical GC conditions and analysis of GC mass spectra against spectral libraries and known compound (class) fragmentation pathways (36). Gas products for GC/MS analysis were collected in an impinger containing 30 mL of methylene chloride at 0 °C (ice bath). The extracts were subsequently concentrated to 1 mL by purge with nitrogen, with analysis via 1.0-μL autoinjection. The reaction product spectrum was compared with standard spectra of the NIST 92 Library (37) and with spectra of purchased standard compounds.

Quantitation from identified polymer oxidation or pyrolysis products is from response factors determined by injection of an external standard, whenever possible. Response factors for products without external standards were assigned according to their carbon number and structure. Detection limits of gas-phase products except CO and CO₂ were at a level of 10–100 ppb.

Results and Discussion

Reactor Operation. Volatilization oven heaters are set to maintain a constant, uniform temperature between 350 and

450 °C. This is below typical grate and fuel-bed temperatures of municipal solid waste incinerators, which are in the approximate ranges 425–540 and 750–1100 °C, respectively (3, 4). This temperature range is chosen to ensure complete and uniform volatilization of polymer feed, with limited further degradation of the initial polymer fragments within the volatilization zone.

The main reactor temperature was initially held at 400 °C. With both the volatilization oven and main reactor at this moderately low temperature, it is assumed that initial polymer fragments leaving the volatilization oven do not undergo significant further reaction or condensation downstream of the volatilization oven and can be analyzed using the on-line GCs. Once this initial product data is obtained, the volatilization oven is maintained at 400 °C and separate experiments are run at main reactor temperatures between 400 and 850 °C in 50 °C intervals.

Exothermicity of the reaction alters the reactor temperature profile slightly. This change is small, less than 10 °C, for the polymers and feed rates in this study. Measured temperature increases due to reaction are below 10 °C in the first 3 cm of the volatilization oven stage and below 3–5 °C in the first 2 cm of the main reactor. There are no other observed changes in the temperature profiles.

Cellulose. Cellulose is a natural biopolymer, with its molecule ($C_6H_{10}O_5$) consisting of approximately 50% oxygen by mass. For this series of runs the carrier gas was dry air, the volatilization oven was maintained at 400 °C throughout, the residence time in the main reactor was a constant 2.0 s, and the fuel equivalence ratio was kept at a fuel-lean value in the range 0.20–0.30. The fuel equivalence ratio for a given run is calculated as the ratio of moles of cellulose (fuel) to oxygen divided by the stoichiometric ratio for the overall reaction: $C_6H_{10}O_5 + 6O_2 \rightarrow 6CO_2 + 5H_2O$. Consideration of the fuel equivalence range and complete reaction for cellulose imply a decrease in the mole percentage of oxygen from 21.6% in inlet air to a value between 14.38% and 16.72% for the reactor effluent.

Initial products from reaction with both the volatilization oven and main reactor temperatures at 400 °C were identified, and 41 species are listed in Table 1. The main pyrolysis products are anhydro sugars, pyran derivatives, alkylfurans, hydrocarbons, and carbonyl compounds. Cellulose in the volatilization oven undergoes dehydration, decarboxylation, transglycosylation, and fission to produce major anhydro sugars such as levoglucosan as well as low-molecular-weight products such as CO, CO₂, methane, ethene, acetaldehyde, furans, acetone, and 2-furfural. These product distributions are in agreement with the thermal decomposition mechanism for cellulose proposed by Pouwels et al. (12) and Shafizadeh (14).

Levoglucosan is one of the primary products and is present at 2% at 400 °C and 2-s reaction time; its concentration is reduced to below its detection limit as the main reactor temperature is increased to 500 °C. It is difficult to analyze levoglucosan with a GC due to its low volatility and interference with other anhydro sugars and oligosaccharides (38–40). The mass balance deficit in Table 1 is attributed to the production of these sugars, which are believed to be major pyrolysis products (41) and accumulate in the reactor's condensation trap (see Figure 1) at low temperatures. 5-(Hydroxymethyl)-2-tetrahydrofurfural-3-one, 5-(hydroxymethyl)-2-furfural, and 1,4:3,6-dihydro- α -D-glucopyranose are initial products from dehydration and transglycosylation reactions. These C₆ oxygenated products are destroyed at temperatures of 500 to 600 °C as indicated by increased carbon mass balance above 500 °C and destruction of the C₅ and higher-molecular-weight products at 600 °C (C₁ to C₄ species, methylfuran, 2-furfural, and aromatic compounds are exceptions). Carbon balance is 88.18% at 600 °C, relative

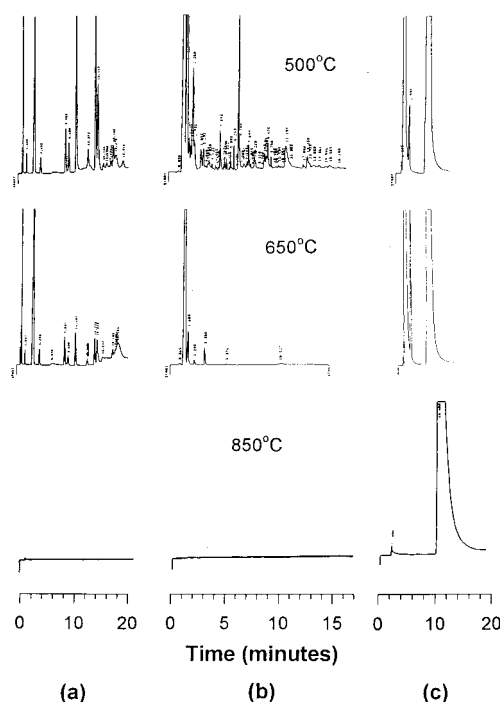


FIGURE 4. Cellulose decomposition product data from the on-line GCs at main reactor temperatures of 500, 650, and 850 °C at 2.0-s residence time: (a) Super-Q column, (b) AT-5 capillary column, (c) Carbosphere column.

to 82.40% at 550 °C and 73.68% at 500 °C. All aromatic compounds disappear at 650 °C, with the exception of benzene, which is present at trace levels at 700 °C. No intermediate or incomplete products of cellulose combustion were detected above 700 °C.

Gas chromatograms from the three different columns are shown at main reactor temperatures of 500, 650, and 850 °C and 2.0-s residence time in Figure 4. This provides a clear picture of the overall product concentrations and their change with temperature. At 400 and 500 °C light hydrocarbons from C₁ to C₄ (Super-Q column) and heavy organic products (AT-5 capillary column) were relatively abundant, while CO and CO₂ (Carbosphere column) were low. At temperatures above 650 °C higher-molecular-weight organic compounds were low and their levels were barely detectable. Light hydrocarbon concentrations began to show rapid falloff, and CO and CO₂ levels increased, as expected. An overall conversion of higher-molecular-weight cellulose polymer fragments to lower-molecular-weight fragments is observed with increasing reaction temperature. The volatilization oven temperature, inlet carrier gas composition, and main reactor residence times were all held fixed, and fuel equivalence was also near-constant. Initial polymer fragment concentrations and compositions entering the main reactor were thus the same throughout.

Figure 5a shows product yields versus temperature for three intermediate molecules: 2-butanone, 2-methylfuran, and 2-furfural. Data for these species show that falloff in concentration begins near 450 °C for 2-butanone and 2-methylfuran, which is lower than the fall-off temperature for C₁ to C₄ species. A major stable product is 2-furfural produced from ring cleavage of levoglucosan via transglycosylation and dehydration. The data show 2-furfural remains as one of the higher level initial products with molecular weight above C₅, from 500 to 600 °C, and that it decreases to near-zero detection level at 650 °C.

Figure 5b illustrates product yields for the C₁ to C₄ species: methane, ethene, acetaldehyde, acetone, and furan versus temperature. Increase in temperature to 650 °C in the

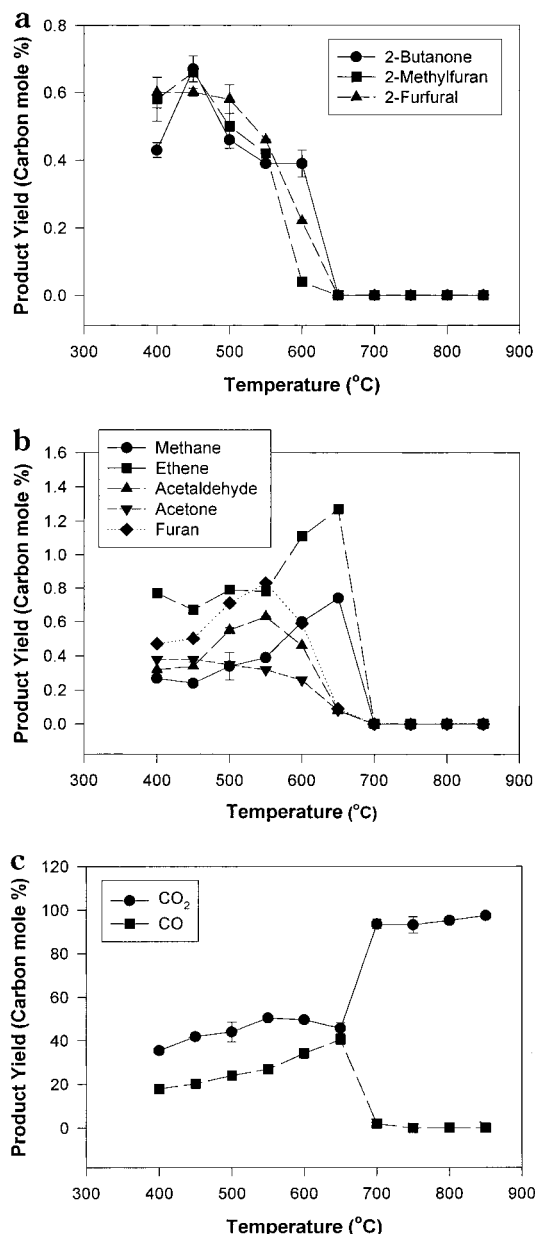


FIGURE 5. Product yields versus main reactor temperature in the thermal oxidation of cellulose: (a) C₄ and C₅ major products, (b) C₁ to C₄ light hydrocarbons, (c) CO and CO₂.

main reactor results in increased concentrations of light hydrocarbons methane and ethene, followed by a rapid falloff at higher temperatures. This trend is consistent throughout our data for cellulose. A similar trend, but with concentration maxima being reached at lower temperatures of 550 °C, is seen for two of the heavier species within this group, acetaldehyde and furan. Concentrations of all species in this group are below detection limits at and above 700 °C.

Product yields for CO and CO₂ are illustrated in Figure 5c as percentage of moles of carbon in the product relative to moles of carbon in the cellulose feed. We note that CO is used as an indicator for complete destruction of PICs in municipal solid waste incinerators, since CO is a stable compound. In this study CO persists at 1.99% at 700 °C, but at our fuel-lean equivalence ratios the concentration of CO is always below that of CO₂. This implies that CO₂ may be produced directly from unimolecular decomposition of the cellulose structure and/or anhydro sugars at low temperature. Complete conversion of other organics through CO to CO₂

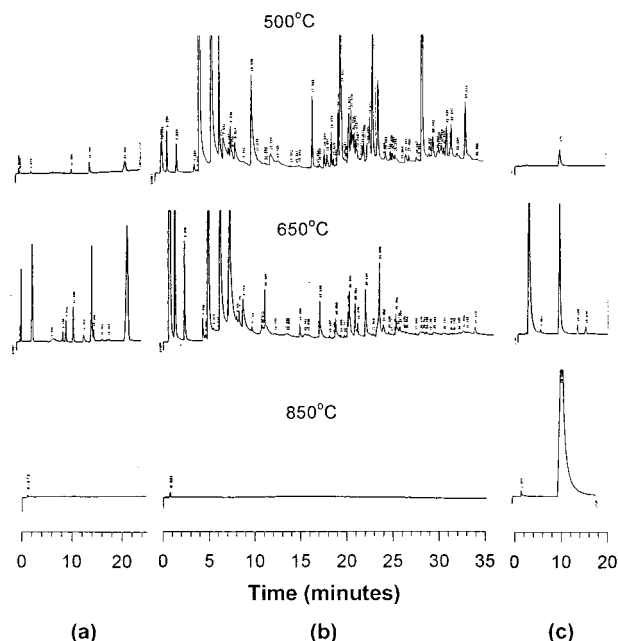


FIGURE 6. Polystyrene decomposition product data from the on-line GCs at main reactor temperatures of 500, 650, and 850 °C at 2.0-s residence time: (a) Super-Q column, (b) DB-1 capillary column, (c) Carboxsphere column.

occurs rapidly between 650 and 700 °C at which CO is oxidized to CO₂.

Polystyrene. Polystyrene is a nonoxygenated vinylphenyl polymer with monomer formula C₈H₈. The experiments were performed at lean fuel equivalence ratios over the range 0.07–0.13, based on the overall reaction: C₈H₈ + 10O₂ → 8CO₂ + 4H₂O. At these equivalence ratios and assuming complete reaction, the mole percentage of oxygen in inlet air decreases from 21.6% to a value between 18.73% and 20.07% in the reactor effluent; 52 species are positively identified by GC and GC/MS analysis, and data are presented in Table 2. Most products show structures related to aromatic monomer, dimer, and trimer of styrene. Initial primary products at 400 °C are predominantly styrene: monomer, dimer, trimer, and benzaldehyde. Minor initial products at 400 °C are CO₂, benzene, toluene, ethylbenzene, α-methylstyrene, 2,3-dihydro-1*H*-inden-1-one, 3-phenyl-2-propen-1-ol, 1,1'-(1,3-propanediyl)bisbenzene, (*E*)-stilbene, 1,1'-(1-butene-1,4-diyl)bis-(*Z*)-benzene, 1,1'-(1,2-ethanediyl)bis-4-methylbenzene, 1,3-diphenyl-(*E*)-2-propen-1-one, *trans*-1,2-dibenzoyl ethylene, and quaterphenyl. Secondary products such as phenylethyne, benzofuran, 1,3-benzodioxole, naphthalene, and biphenyl result from oxidation and pyrolysis of initial products in the main reactor zone. These species are relatively low in concentration at 400 °C, where they are detected by GC/MS analysis only, but their concentrations increase with increasing main reactor temperature.

Figure 6 shows GC chromatographic data for temperatures of 500, 650, and 850 °C at 2.0-s residence time. The trends show a clear increase in conversion of high-molecular-weight intermediates to lower-molecular-weight products (similar to results found for cellulose) as main reactor temperature is increased. The change in the distribution of product concentrations with temperature is dramatic and demonstrates that the aromatic products formed in the thermal oxidation of polystyrene can be degraded under these fuel-lean 700–850 °C conditions.

Polystyrene radical is formed by chain-end and random β-scission (elimination reactions) at weak bonds (adjacent to radical sites) in the polymer chain, as reported by several researchers (42–45). Styrene is produced from β-scission of

TABLE 2. Distribution and Fate of Vapor-Phase Products in the Oxidation of Polystyrene^a

no.	MW	products	main reactortemperature (°C)								
			400	450	500	550	600	650	675	700	750
1	16	methane, CH ₄	x	x	x	x	x	x	x	x	
2	28	ethene, C ₂ H ₄			x	x	x	x	x		
3	42	propene, C ₃ H ₆					x	x	x		
4	44	acetaldehyde, C ₂ H ₄ O		x	x	x	x	x	x		
5	56	butene, C ₄ H ₈				x	x	x	x		
6	56	acrolein, C ₃ H ₄ O		x	x	x	x	x	x		
7	58	acetone, C ₃ H ₆ O				x	x	x	x		
8	78	benzene, C ₆ H ₆	x	x	x	x	x	x	x		
9	92	toluene, C ₇ H ₈	x	x	x	x	x	x	x		
10	106	ethylbenzene, C ₈ H ₁₀	x	x	x	x	x	x	x		
11	102	phenylethyne, C ₈ H ₆	+		x	x	x	x			
12	104	styrene, C ₈ H ₈	x	x	x	x	x	x	x		
13	106	benzaldehyde, C ₇ H ₆ O	x	x	x	x	x	x	x		
14	118	α-methylstyrene, C ₉ H ₁₀	x	x	x	x	x	x			
15	118	benzofuran, C ₈ H ₁₀ O	+		x	x	x	x	x		
16	122	1,3-benzodioxole, C ₇ H ₆ O	+	x	x	x	x	x			
17	120	benzeneacetaldehyde, C ₈ H ₈ O	x	x	x	x	x	x			
18	116	indene, C ₉ H ₁₀	x	x	x	x	x	x			
19	132	3-butenylbenzene, C ₁₀ H ₁₂	+								
20	148	1-phenyl-1,2-propanedione, C ₉ H ₈ O ₂	x	x	x	x	x	x			
21	132	1-(methylenepropyl)benzene, C ₁₀ H ₁₂	+					x			
22	132	2,3-dihydro-1 <i>H</i> -inden-1-one, C ₉ H ₈ O	x	x	x	x	x	x			
23	122	benzoic acid, C ₇ H ₆ O ₂	+								
24	128	naphthalene, C ₁₀ H ₈	+		x	x	x	x	x		
25	132	2-methylbenzofuran, C ₉ H ₈ O	+								
26	134	3-phenyl-2-propen-1-ol, C ₉ H ₁₀ O	x	x	x	x					
27	132	3-phenyl-2-propanal, C ₉ H ₈ O	+								
28	154	biphenyl, C ₁₂ H ₁₀	+		x	x	x	x			
29	168	diphenylmethane, C ₁₃ H ₁₂	+								
30	180	1,1'-diphenylethylene, C ₁₄ H ₁₂	x	x	x	x	x	x	x		
31	182	bibenzyl, C ₁₄ H ₁₄	+								
32	194	α-methyl-(<i>E</i>)-stilbene, C ₁₅ H ₁₄	x	x	x	x	x				
33	180	4-ethenyl-1,1'-biphenyl, C ₁₄ H ₁₂	x	x	x	x	x	x			
34	182	benzophenone, C ₁₃ H ₁₀ O	+								
35	196	1,1'-(1,3-propanediyl)bisbenzene, C ₁₅ H ₁₆	x	x	x	x	x				
36	180	9,10-dihydrophenanthrene, C ₁₄ H ₁₂	+								
37	180	(<i>E</i>)-stilbene, C ₁₄ H ₁₂	x	x	x	x	x	x			
38	208	styrene, dimer, C ₁₆ H ₁₆	x	x	x	x	x	x	x		
39	194	1-methyl-2-(2-phenylethenyl)benzene, C ₁₅ H ₁₄	x	x	x	x	x				
40	178	anthracene, C ₁₄ H ₁₀	x	x	x	x	x	x	x		
41	206	1,4-diphenyl-1,3-butadiene, C ₁₆ H ₁₄	x	x	x	x	x				
42	208	1,1'-(1-butene-1,4-diyl)bis-(<i>Z</i>)-benzene, C ₁₆ H ₁₆	x	x	x	x	x				
43	210	1,1'-(1,2-ethanediyl)bis-4-methylbenzene, C ₁₆ H ₁₈	x	x	x	x	x	x	x		
44	234	<i>cis</i> -4b,5,6,10b,11,12-hexahydrochrysene, C ₁₈ H ₁₈	x	x	x	x	x				
45	204	2-phenylnaphthalene, C ₁₆ H ₁₂	x	x	x	x	x	x	x		
46	208	1,3-diphenyl-(<i>E</i>)-2-propen-1-one, C ₁₅ H ₁₂ O	x	x	x	x	x				
47	222	1-(4-methylphenyl)-3-phenyl-2-propen-1-one, C ₁₆ H ₁₄ O	x	x				x			
48	236	<i>trans</i> -1,2-dibenzoylthylene, C ₁₆ H ₁₂ O ₂	x	x	x	x	x				
49	312	styrene, trimer, C ₂₄ H ₂₄	x	x	x	x	x				
50	306	quaterphenyl, C ₂₄ H ₁₈	x	x	x	x	x	x			
51	28	CO		x	x	x	x	x	x	x	
52	44	CO ₂	x	x	x	x	x	x	x	x	x
fuel equivalence ratio (φ)			0.07	0.07	0.07	0.08	0.09	0.10	0.10	0.10	0.11
carbon mass balance (%)			77.56	78.02	91.17	95.36	92.41	88.59	85.95	88.32	93.73

^a Volatilization oven temperature 400 °C, main reactor temperature as indicated; x signifies detected by GC and GC/MS analysis, + signifies detected by GC/MS and not detected by GC.

chain-end polystyryl radical in propagation reactions. Dimer, trimer, and oligomers of styrene result from intramolecular hydrogen transfers and β-scission reactions. Relative concentrations observed in initial vapor-phase products are monomer > trimer > dimer at 400 °C, as shown quantitatively in Figure 7a. These data are consistent with trends reported by previous researchers (29–31). Maximum product yields for styrene (46.40%) and benzaldehyde (11.89%) are observed at 550 °C. The maxima for styrene trimer (17.51%) and dimer (4.27%) occurred at 400 °C. These major volatilization products of polystyrene are reduced to levels of 0.03% at 600 °C for the trimer, while at 675 °C styrene monomer is 0.96% and the dimer is 0.15%.

2,3-Dihydro-1*H*-inden-1-one is an oxygenated species that appears in relatively high levels at low temperatures and then decreases in intensity at 650 °C. Stilbene, 1-methyl-2-(2-phenylethenyl)benzene, 1,3-diphenyl-2-propen-1-one, and quaterphenyl are also present in the temperature range 400–600 °C but are below detection limits by 675 °C.

Benzene and ethene follow patterns shown in Figure 7b,c; maximum benzene levels of 5.71% occur at 650 °C. C₂ to C₄ compounds show similar results to that of benzene, while ethene is 2.24% at 675 °C. Benzofuran persists at 675 °C, along with naphthalene, 1,1-diphenylethylene, and 2-phenylnaphthalene; these species survive through 675 °C, but only at barely detectable levels. Benzene level decreased rapidly

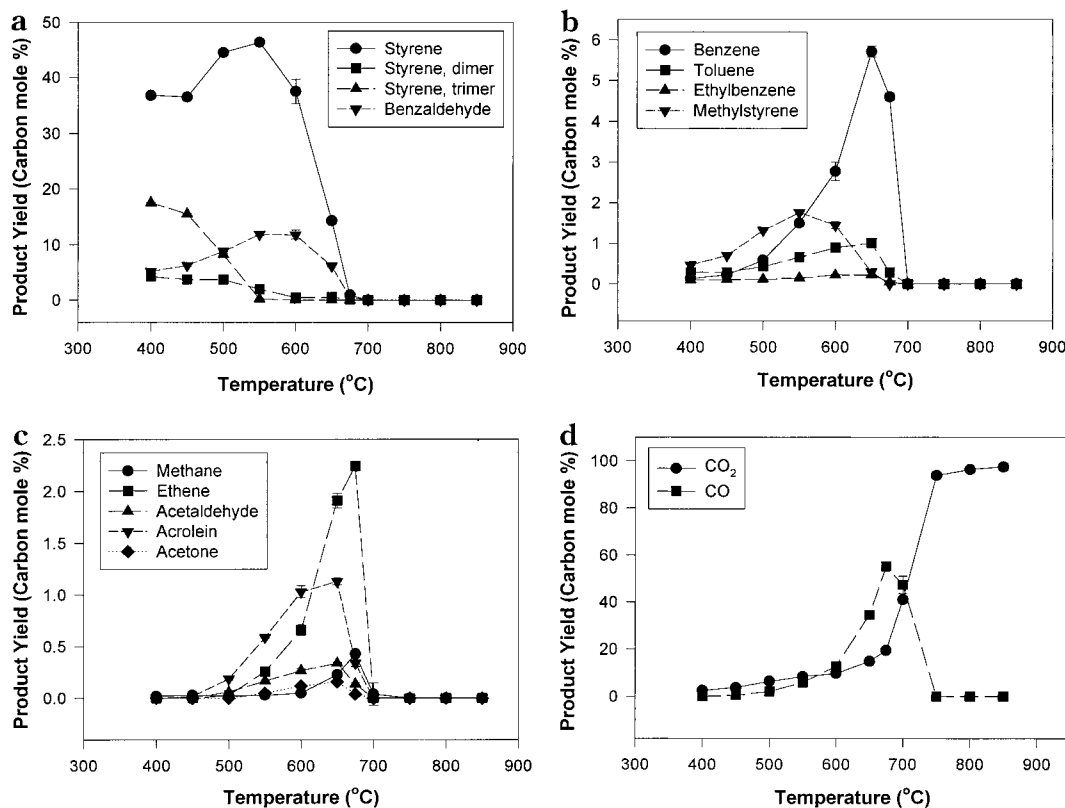


FIGURE 7. Product yields versus main reactor temperature in the thermal oxidation of polystyrene: (a) styrene monomer, dimer, and trimer and benzaldehyde, (b) C₆ to C₉ aromatic hydrocarbons, (c) C₁ to C₄ light hydrocarbons, (d) CO and CO₂.

above 650 °C and was below detection limits at 700 °C and above.

Carbon mass balance at 650 °C is 88.59% and decreases to 85.95% at 675 °C, which is an important temperature for polystyrene oxidation in this study. At this temperature, the levels of more common polyaromatic hydrocarbons, such as indene, naphthalene, biphenyl, benzofuran, and anthracene, are diminished, i.e., present only in very low concentration. High-molecular-weight PAHs with fused ring structures are not observed above 675 °C.

Carbon monoxide and carbon dioxide yields versus main reactor temperature are shown for polystyrene in Figure 7d. CO and CO₂ yields are lower for polystyrene than for cellulose up to reactor temperatures near 650 °C. This is a consequence of higher stability in the polystyrene volatilization products due to conjugation in the styrene and the absence of oxygen in the rings and side chains. Although CO converts to CO₂ at temperatures in the range 650–700 °C for both cellulose and polystyrene, the conversion is less rapid for polystyrene, suggesting a less oxidative radical pool environment. Complete conversion of CO to CO₂ occurs at a temperature of 750 °C for both polystyrene and cellulose.

Overall Polymer Oxidation: Cellulose and Polystyrene. The overall effect of increasing temperature from 400 to 850 °C with other parameters fixed is to reduce higher-molecular-weight intermediates from polymer decomposition for both cellulose and polystyrene, under conditions of fuel-lean equivalence ratio and 2.0-s reaction time. An initial increase in levels of lower-molecular-weight products is observed, followed by their conversion to CO₂ and H₂O as the temperature of complete combustion is approached.

The decomposition products from the two polymers are complex and are representative of the different polymer structures and their respective pathways of decomposition. Cellulose decomposition results in a large variety of complex organic hydrocarbons and oxyhydrocarbon species, while

polystyrene volatilization and oxidation result in aromatic and substituted aromatics. Volatilization products from thermal pyrolysis or oxidation of cellulose and polystyrene are shown to achieve complete combustion to CO₂ and H₂O at temperature of 750 °C under the reaction conditions of this study.

Continuous feed, steady-state reactor operation enables the monitoring of polymer volatilization (initial fragmentation and decomposition), initial and intermediate polymer reaction products, and their concentrations as a function of temperature. These data supplement knowledge of the reaction process provided by batch or drop-tube furnace reactors. It is of value in interpretation of initial volatilization species, both qualitative distribution and concentrations. It also provides quantitative data on fate or conversion versus temperature.

We suggest the use of total hydrocarbon and CO or CO₂ as a continuous monitor relevant to the attainment of uniform operation in these studies. Total HC is a valid monitor of the steady state when operating at low conversion, and CO or CO₂, especially if calibrated for mass balance, is appropriate to higher conversion.

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